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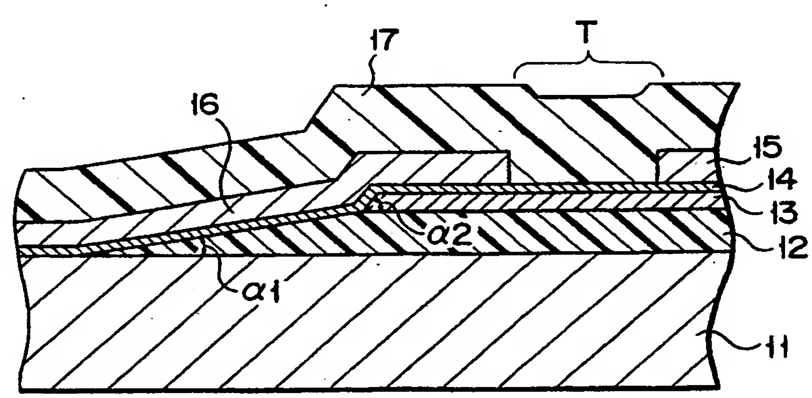
(54) **Method of manufacturing thermal head.**

(57) A method for manufacturing a thermal head comprising the steps of forming a heat resistant resin layer (12) on the surface of a substrate (11), removing a part of the heat resistant resin layer (12) by a photochemical reaction using an excimer laser beam having a wavelength of 150 to 400nm, thereby exposing a part of the substrate (11), forming a heat-generating resistive layer (14), an individual electrode (15) and a conductive layer (16) on the heat resistant resin layer and the exposed part of the substrate (11).



F I G. 2

EP 0 459 481 A2

This invention relates to a method of manufacturing a thermal head having a high resistance substrate comprising a heat resistant resin coating layer as a heat insulating layer.

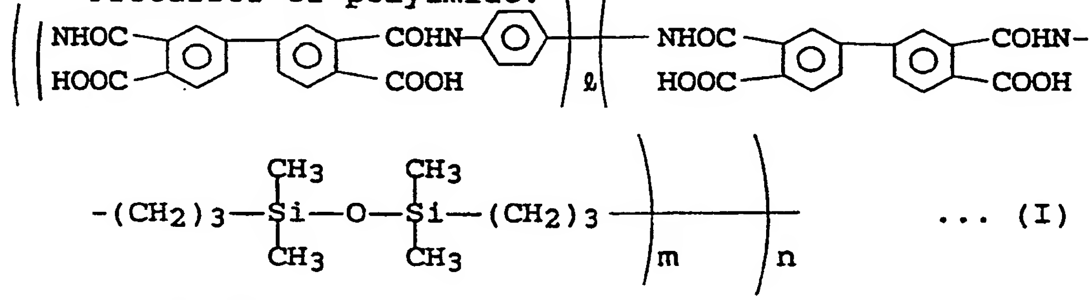
Recent years, a thermal head is utilized for various recording apparatuses such as a facsimile, a printer for a word processor, or the like, on account of the advantages of noiseless, no need of in maintenance, a low running cost, etc. It is desirable that these recording apparatuses be compact, inexpensive, and low power consuming. Accordingly, a compact, inexpensive, and high-efficient thermal head has been required.

To meet the requirements, as disclosed in Published Unexamined Japanese Patent Application (PUJPA) No. 52-100245, it is proposed to use, as a heat-insulating layer of a thermal head, a resin layer (e.g., polyimide or epoxy resin) having a small thermal conductivity, instead a glazed glass layer conventionally used.

The above-described polyimide layer was difficult to use for a thermal head in practice, since it is difficult to obtain a resin which can be used for the polyimide layer 2 serving as a heat insulating layer in the thermal head, i.e., a resin which has such heat resistance and adhesion enough to withstand the operation of the thermal head.

The present inventors developed aromatic polyimide having the following molecular structure, and opened a prospect for realizing a thermal head having a heat insulating layer made of resin (see USP 4868584).

Precursor of polyimide:



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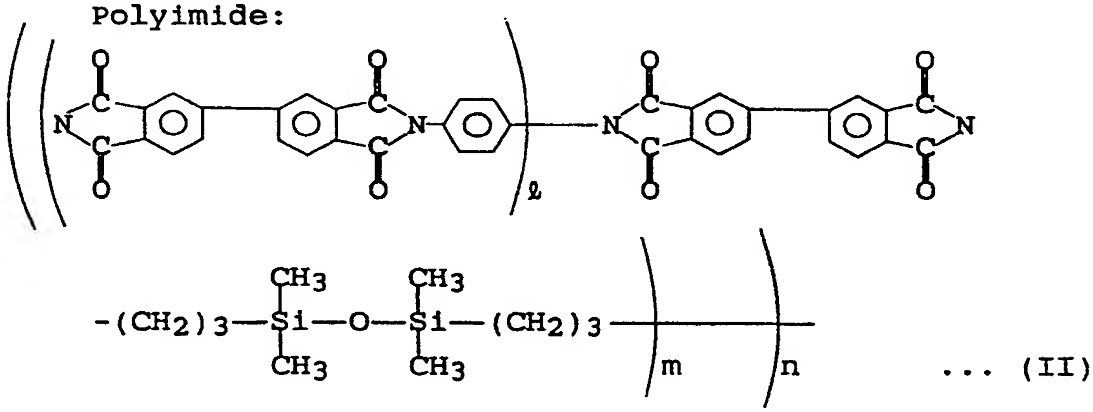
Polyimide:



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The polyimide is formed as follows: a ring-opening poly-addition reaction is performed using a equimolar mixture of a biphenyl tetracarboxylic acid dihydride and a p-phenylene diamine, 0.05 to 10 mol% of p-phenylene diamine being replaced by bisaminosiloxane, to produce a polyamic acid; and the polyamic acid is coated on a metal substrate and baked, thereby forming a polyimide layer on the substrate. The polyimide layer not only enables the thermal head to operate at a high efficiency but also provides a high characteristic in image quality. Similar polyimide resins are described in the Summary of SPSE's 5th International Congress on Advances in Non-Impact Printing Technologies, page 261 (November 12, 1989).

Fig. 1 is an example of the above-mentioned thermal head.

As is shown in Fig. 1, the thermal head includes a metal substrate 1, on which a polyimide layer 2 is formed. A resin protecting layer 3 is formed on the polyimide layer 2 to protect polyimide from CDE (Chemical Dry Etching) and ashing, to control the resistance of a heat-generating resistive layer (which will be formed later) easily, and to prevent a crack which may be caused by foreign material rolled up by the thermal head having a resin layer serving as a heat insulating layer.

A heating resistor 4 made of Ta-SiO2, Nb-SiO_2 and the like is formed on the resin protecting layer 3. An individual electrode 6 and a common electrode 7 made of Aℓ, Aℓ-Si-Cu and the like are formed on the heat-generating resistor so as to form an opening to serve as a heat-generating portion 5. In this manner, the heating portion 5 is formed. Further, a protecting layer 8 made of Si-O-N, Si-Aℓ-O-N, Si-Zr-Y-N-O, and the like is formed so as to cover at least the heat-generating portion 5.

The above-mentioned thermal head, which comprises a high-resistance substrate having a metal substrate and a resin layer formed thereon, has the following advantages and is expected to be a high performance thermal head of a next generation.

i) Since the thermal head is easy to bend and its shape or configuration can be varied more freely, it is possible to form a compact head or be used as a vertical type head.

ii) The metal substrate can be used as a common electrode by patterning the resin layer serving as a heat insulating layer. Thus, a common electrode can be formed in a simple step, thereby lowering the entire manufacturing cost.

To use as a common electrode the metal substrate in the high resistance substrate, patterning of the polyimide layer formed on the metal substrate is unavoidable as described above. The process of patterning is complicated, which makes the patterning unsatisfactory in accuracy and cost.

One of the methods of patterning a resin on a metal substrate for forming a common electrode using a metal substrate is to print polyamic acid on the metal substrate into a predetermined pattern by a screen printer. In this method, a filler must be added to polyamic acid to control the thixotropy and the viscosity to obtain a paste suitable for the printing. Such a paste cannot provide the above-described advantages of a heat resistant layer made of polyimide. In addition, an unprinted portion of the metal substrate which should serve as a common electrode may be oxidized by an oxide gas generated during the dehydrating cyclizing reaction, with the result that an insulting layer is formed on that portion.

Another method of patterning a resin layer is to plate a portion of the metal substrate surface with a metal which is not easily adhesive to polyimide and are not oxidized easily (e.g. Pt, Pd, and Au), coat a resin layer on the substrate using the plated portion, and remove the plated portion. This method requires complicated manufacturing processes and high cost.

Whether the patterning is performed in the former or latter method, the thermal head as shown in Fig. 1 requires an insulating layer, i.e., a ceramic film serving as a resin protecting layer. Hence, it is also necessary to form a pattern for the ceramic film.

Moreover, the edges of the pattern form an angle of about 90°C with the substrate. Hence, step coverage of the thin resistor film and conductive film on the edge is deteriorated to cause disconnection of these films. To prevent the failures and to reliably connect the resin layer (heat insulating layer) with a conductive film formed directly or indirectly over the resin layer, it is desirable to form sloped edges having suitable angles. It is also desirable that the portion of the metal substrate exposed by patterning be clean.

No conventional methods could satisfy the above-mentioned requirements. A preferable patterning method for using the metal substrate as a common electrode has been awaited.

The present invention has been conceived to overcome the above-described problems of the conventional art, and its object is to provide a method of manufacturing a thermal head using a high resistance substrate having a metal substrate and a heat resistant resin layer formed thereon, wherein patterning of the resin layer to form a common electrode using the metal substrate is satisfactorily performed, and the property of the resin layer is fully utilized, thereby improving the quality of the product.

A method of manufacturing a thermal head according to the present invention comprises the steps of:

forming a heat resistant resin layer on a substrate;

removing a portion of the heat resistant resin layer by photochemical reaction by means of excimer laser which emits beams having a wavelength of 150 to 400nm, thereby exposing the portion of the substrate;

forming a heating resistor layer on the heat resistant resin layer and the exposed portion of the substrate; and

forming a conductive film and an individual electrode on the heating resistor layer.

According to the present invention, it is possible to simultaneously remove the heat resistant resin layer and an unneeded oxide layer formed between the metal substrate and the resin layer by means of excimer laser beams having the above-mentioned wavelength.

Since it is unnecessary to process resin material to form a heat resistant resin layer, the property of the resin material is not degraded, and a heat resistant resin layer of a desirable property can be formed. In addition, since the heat resistant resin layer is removed basically by photochemical reaction rather than heat, alteration by heat is prevented. Furthermore, if the edges of the heat resistant resin layer formed by the laser beams are tapered, sufficient step coverage of the heating resistor layer with the conductive film

thereon can be obtained. Hence, the heat resistant resin layer and layers formed thereon are not easily disconnected.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a cross sectional view showing a conventional thermal head having heat resistant resin layer as a heat insulating layer;

Fig. 2 is a cross sectional view showing a thermal head formed by a method of an embodiment of the present invention;

Fig. 3 is a diagram showing a patterning device using an excimer laser; and

Fig. 4 is a cross sectional view showing a thermal head formed by a method of another embodiment of the present invention.

The thermal head of the present invention is manufactured as follows.

First, as is shown in Fig. 2, a heat resistant resin layer 12 is formed on a substrate 11. It is desirable that the substrate 11 be formed of a metal substrate made of Fe-Cr, Fe-Cr-Nb, and the like, a ceramic substrate made of Al_2O_3, AlN and the like or glassy epoxy substrate. These ceramic and glassy epoxy substrates have a metal film thereon as a common electrode and the like. Also, it is desirable that the heat resistant resin layer 12 be formed of one selected from the group consisting of polyimide, polyamide-imide and polyamide. A protecting layer 13, which is made of, for example, an in organic materials such as SiOx, SiCx, SiNx, Si-Al-O-N, Si-Zr-O-N or the like, may be formed on the heat resistant resin layer 12.

Predetermined portions of these layers formed on the substrate body 11 are removed by a photochemical reaction using an excimer laser beam having a wavelength of 150 to 400nm. A heating resistor layer 14, which is made of, for example, Ta-SiO_2, Nb-SiO_2, Cr-SiO_2, or the like, is formed on top of the substrate body 11.

Thereafter, an individual electrode 15 and a conductive film 16, made of, for example, Al, are formed on predetermined portions of the heating resistor layer 14. More preferably, a protecting layer 17 is formed so as to cover the entire surface, thus accomplishing a thermal head. The protecting layer 17 is made of, for example, Si-O-N, Si-Zr-Y-O-N, SiCx, or the like.

As excimer lasers which emit beams having a wavelength of 150 to 400nm, an ArF excimer laser, a KrF excimer laser, an XeCl excimer laser, and an XeF excimer laser are known, which respectively emit beams having wavelengths of 193nm, 248nm, 308nm, and 353nm. The most preferable wavelength of the excimer laser beams is 200 to 360 nm.

Excimer laser beams of a wavelength shorter than 150nm are disadvantageous in practical use in that penetration depth of beams into the heat resistant resin layer is extremely shallow, thus requiring a long period of time to remove a portion of the resin layer. On the other hand, excimer laser beams of a wavelength longer than 400nm are disadvantageous in practical use in that the surface of the edges processed by the laser beams is rough.

Since an excimer laser exited by ultraviolet rays, which has a wavelength shorter than those of visible and infrared lasers, to cause oscillation, one photon has energy greater than that of visible and infrared lasers. In the laser beam irradiating portion, photons of excimer laser beams directly excite a chemical bond of polyimide to dissociate, which is considered to be gradually changed to a form which is easily vaporized in accordance with the dissociation. Vaporization proceeds by heat as the change of polyimide, resulting in a sharp edge which has not been affected by heat.

If a resin protecting layer is formed on the heat resistant resin layer, it can be removed together with the heat resistant resin layer in the removing step. It is desirable that the edge of the heat resistant resin layer processed by excimer laser beams form a taper angle α_1 ($3^\circ < \alpha_1 < 40^\circ$) to the substrate surface, and that the edge of the resin protecting layer form a taper angle α_2 ($30^\circ < \alpha_2 < 50^\circ$) to the substrate surface. The taper angles α_1 and α_2 can be changed by controlling energy distribution of the excimer laser beam.

According to the present invention, excimer laser beams having a wavelength of 150nm to 400nm is used to remove portions of the heat resistant resin layer by a photochemical reaction. It is possible to simultaneously remove the resin protecting layer formed on the heat resistant resin layer and an unneeded oxide layer formed between the metal substrate and the resin layer by the excimer laser beams having the above-mentioned wavelength.

Since it is unnecessary to process resin material to form a heat resistant resin layer, the property of the resin material is not degraded, and a heat insulating layer of a desirable property can be formed. In addition, since the resin protecting layer is removed basically by a photochemical reaction rather than heat, adverse effect by heat is prevented.

According to the present invention, it is assumed that polyimide is removed in the following manners.

i) When an excimer laser irradiates polyimide, a bond C-N absorbs photons of the laser beams, and is excited to be cleaved, thereby dissociating and removing polyimide.

ii) When an excimer laser irradiates polyimide with greater energy, C-N, C-C, C-O, and C-H bonds are cleaved, thereby destructing cyclic imide and a straight chain. Thus, polyimide is dissociated into monomers and removed.

In these manners, since energy of the laser beams is used for cleavage of bonds, effect of heat to the thermal head is decreased.

As described above, since excimer laser beams having a wavelength of 150nm to 400nm is used to remove portions of the heat resistant resin layer by a photochemical reaction, a thermal head having a satisfactory property of the heat resistant resin which is not affected by heat is obtained without processing resin material.

The following are examples according to the method of the invention.

Example 1

Fig. 2 shows Example 1. As shown in Fig. 2, a metal substrate 11 having a thickness of 0.5mm and formed of an Fe alloy containing 18 wt% of Cr is subjected to a leveling process, and cut in a predetermined size, and deburring is performed.

The metal substrate 11 is cleaned with alcohol and thereafter subjected to optical cleaning with UV/O_3.

Subsequently, the metal substrate 11 is immersed in, for example, an aqueous solution having a temperature of 40 to 60°C containing 5 to 20 vol% of 96% H_2SO_4 for 1 to 2 minutes, thereby removing the oxide layer, including Cr_2O_3 as its main component, formed on the metal substrate 1, and making the substrate surface rough. This process is referred to as an activating process. After the activating process, an organic solvent such as N-methyl-2-pyrolidone (NMP) was added to a polyamic solution which is a precursor of polyimide, thereby obtaining a desired viscosity. The solution thus obtained is deposited to the metal substrate 11 to a predetermined thickness by using a roll coater or a spin coater. Then, the substrate is baked in nitrogen gas within a baking furnace under the conditions of 50°C for 60 minutes, 80°C for 30 minutes, 250°C for 60 minutes, and 450°C for 30 minutes in sequence, thereby removing the organic solvent. At the same time, dehydrating cyclizing reaction proceeds and the precursor is changed to polyimide, thereby forming a heat resistant resin layer 12 having a thickness of about 20 μm. Meanwhile, an oxidizing gas such as H_2O gas generated by the dehydrating cyclizing reaction oxidizes the surface of the metal substrate 11, thereby reliably adhering the metal substrate 11 and the heat resistant resin layer 12.

Next, an Si-Zr-Y-N-O film serving as a resin protecting layer 13 is formed on the heat resistant resin layer 12 by sputtering method to a predetermined thickness. Then, the heat resistant resin layer 12 is patterned by a device shown in Fig. 3. As shown in Fig. 3, an excimer laser 20 emits excimer laser beams having a wavelength of 150 to 400nm. The laser beams are cut into a predetermined size by an aperture 21, reflected at a predetermined angle by, for example, a dichroic mirror 23, then converged by a quartz lens 24 set to a suitable focal distance, and applied to the metal substrate coated with the resin which is fixed to an X-Y table 25. An X-Y control board is provided to the X-Y table 25 to move the X-Y table to a desired position to control the radiation position and the radiation angle of the laser beams.

In this example, a KrF excimer laser which emits beams having a wavelength of 248nm is used. By the process using the laser, the edge of the heat resistant resin layer 12 is tapered at an angle $\alpha_1 = 5^\circ$, and the edge of the resin protecting layer 13 is tapered at an angle $\alpha_2 = 30^\circ$.

To remove material such as carbon which is adhered to the resin protecting layer 13 due to the photochemical reaction by the laser beams, the substrate is scraped with neutral detergent, rinsed in pure water, subjected to substitution using isopropyl alcohol, and thereafter dried.

A heating resistor film 14 made of Ta-SiO_2 is formed on the resin protecting layer 13. Subsequently, an Aℓ layer is formed on the entire substrate. A resist layer is formed on the Aℓ layer. The Aℓ layer is patterned into a predetermined configuration by photolithography technique, thereby forming an individual electrode 15 and a conductive film 16 made of aluminum. The conductive film 16 electrically connects the metal substrate serving as a common electrode with the heating resistor film 14.

Then, the masking film is removed and a protecting layer 17 made of Si-Zr-Y-N-O is formed on the substrate so as to cover the heating portion T. Thus, a thermal head is obtained.

The thermal head obtained in this manner was placed in an atmosphere of high temperature and humidity containing 95% of RH at a temperature of 40°C for 1,000 hours. Thereafter, a Cross Cut Tape Test (ASTM) was performed, with the result that peeling was not observed in the heat resistant resin layer 12 and no problem occurred in practical use.

Example 2

Fig. 4 is a cross sectional view showing a thermal head according to another embodiment of the present invention.

The thermal head of this embodiment has the same structure as in Example 1 except that an a-SiC_x layer 13a and an a-SiO_x layer 13b constituting a resin protecting layer are formed by plasma CVD method.

Also, this example differs from Example 1 in that an XeCℓ excimer laser which emits laser beams having a wavelength of 308nm is used, and the edge of the heat resistant resin layer 12 is tapered at an angle α_3 = 6° and the edge of the resin protecting layer is tapered at an angle of α_4 = 40°

The thermal head thus formed was subjected to the Cross Cut Tape Test in the same conditions as in Example 1, with the result that the heat resistant resin layer was not removed and no problem occurred in practical use.

Example 3

A thermal head of this embodiment has the same structure as in Example 1 except that a glassy epoxy or a ceramic substrate with a conductive film formed thereon as a common electrode is used as a substrate.

Also, this embodiment differs from Example 1 in that the edge of the heat resistant resin layer 12 is tapered at an angle α_5 = 10° and the edge of the resin protecting layer is tapered at an angle of α_6 = 35°.

The thermal head thus formed was subjected to the Cross Cut Tape Test in the same conditions as in Example 1, with the result that the heat resistant resin layer was not removed and no problem occurred in practical use.

The conditions and effects of Examples 1, 2 and 3 are shown in Table 1.

Table 1

Conditions	Example 1	Example 2	Example 3
thickness of polyimide layer	20 μm	20 μm	20 μm
thickness of protecting layer	3.5 μm	6 μm	3 μm
laer	KrF	XeCℓ	XeCℓ
wavelength of laser beams	248nm	308nm	308nm
energy density	1.9J/cm^2	1.2J/cm^2	2.0J/cm^2
frequency	100 Hz	100 Hz	100 Hz
traveling speed	10mm/sec	10mm/sec	10mm/sec
diameter of beam spot	2mmφ	2mmφ	2mmφ
taper angle (α) of resin layer	α_1 = 5°	α_3 = 6°	α_5 = 10°
taper angle (α) of resin protecting layer	α_2 = 30°	α_4 = 40°	α_6 = 35°
cross cut test	not peeled	not peeled	not peeled

In Example 2, a-SiO_x forming the resin protecting layer is transparent to excimer laser beams having a wavelength of 150 to 400nm. If two layers can be removed by a photochemical reaction by using excimer laser beams, a transparent layer interposed between the two layers can also be processed. More specifically, first, excimer laser beams remove the uppermost layer (a-SiC_x layer), pass through an intermediate transparent layer (a-SiO_x layer), and reach the lowermost layer (polyimide layer). When the

lowermost layer begins to be removed by photochemical reaction, gas begins to generate. As a result, the exposed portion of the intermediate layer is raised by the pressure of the gas, and the exposed portion of the intermediate layer is removed as if the intermediate layer is cut by a cutting knife at the portion between the edges of the uppermost layer and lowermost layer processed by the excimer laser.

As has been described above, since the heat resistant resin layer is basically removed by a photochemical reaction, rather than heat, a satisfactory thermal head having a desirable property which is expected in a case of using a heat insulating layer made of a heat resistant resin is obtained with no heat affected part.

Claims

1. A method for manufacturing a thermal head comprising the steps of:
   forming a heat resistant resin layer (12) on the surface of a substrate (11);
   forming a heat-generating resistive layer (14) on said heat resistant resin layer (12); and
   forming an individual electrode (15) and a conductive film (16) on said heat-generating resistive layer (14),
   characterized by further comprising, before said step of forming the heat-generating resistive layer (14), the step of removing a part of said heat resistant resin layer (12) by a photochemical reaction using an excimer laser beam having a wavelength of 150 to 400nm, thereby exposing a part of said substrate (11).

2. A method according to claim 1, characterized by further comprising the step of forming a resin protecting layer on said heat resistant resin layer, characterized in that a part of said resin protecting layer is also removed in the step of removing the part of said heat resistant resin layer.

3. A method according to claim 1, characterized in that an edge of said heat resistant resin layer processed by the excimer laser forms a taper angle α_1 ranging from 3° to 40° with the surface of said substrate.

4. A method according to claim 1, characterized in that an edge of said resin protecting layer processed by the excimer laser forms a taper angle α_2 ranging from 30° to 50° with the surface of said substrate.

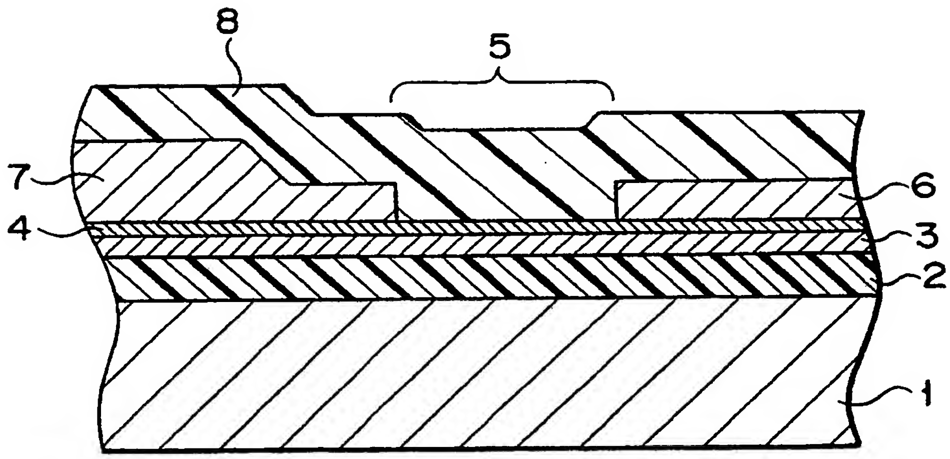
5. A method according to claim 1, characterized in that the wave length of the laser is 200 to 360nm.

6. A method according to claim 1, characterized in that said substrate is made of metal.

7. A method according to claim 1, characterized in that said substrate is a ceramic substrate having a conductive film thereon or a glassy epoxy substrate having a conductive film thereon.

8. A method according to claim 7, characterized in that said ceramic is selected from the group consisting of $A\ell_2O_3$ and $A\ell N$.

9. A method according to claim 1, characterized in that said heat resistant resin layer is made of one selected from the group consisting of polyimide, polyamide-imide, and polyamide.



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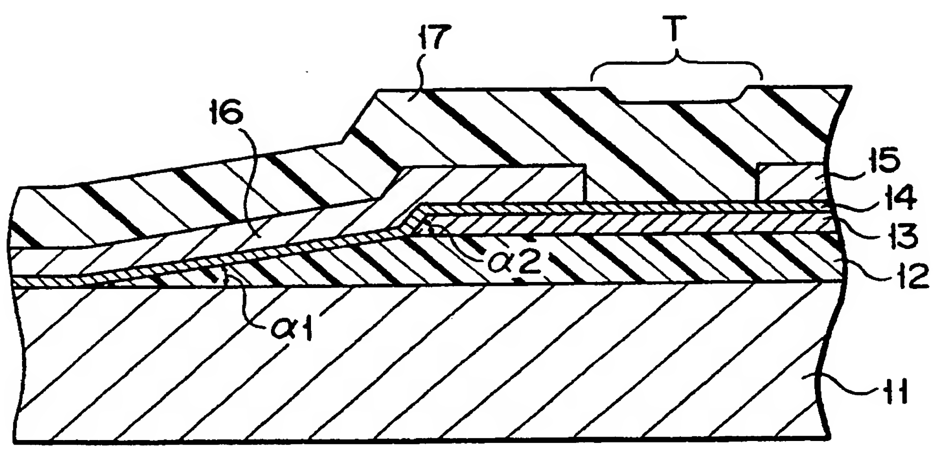
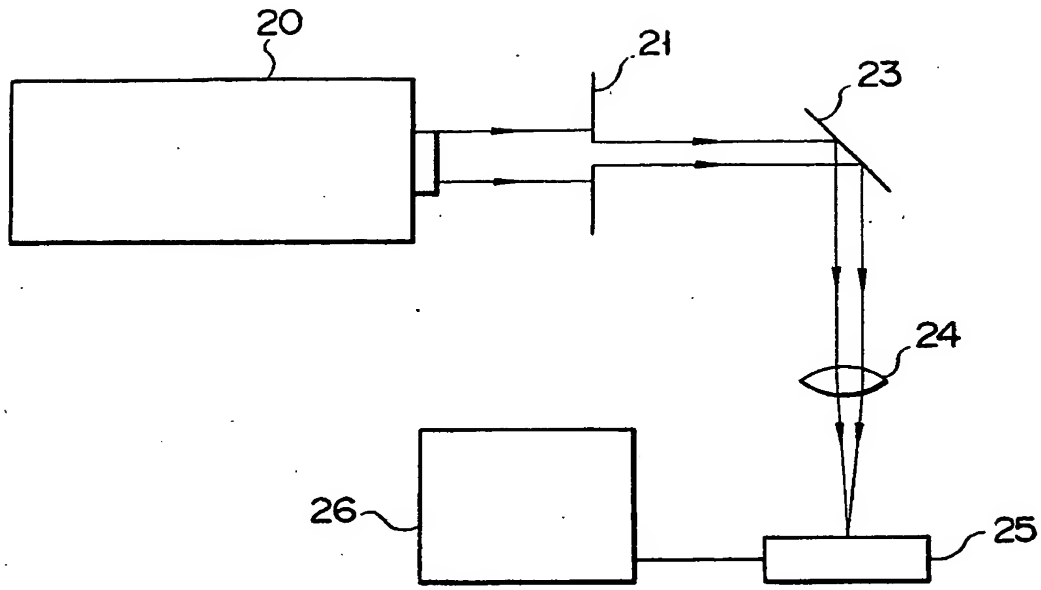


F I G. 2



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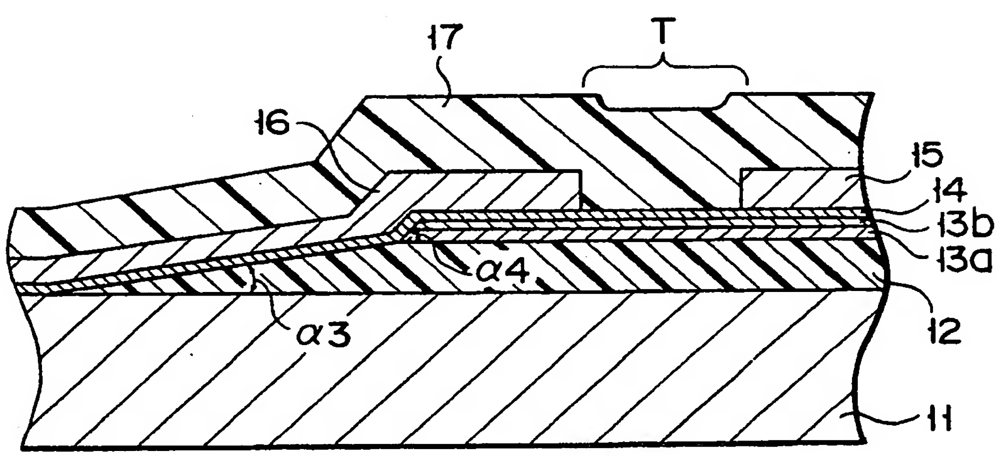

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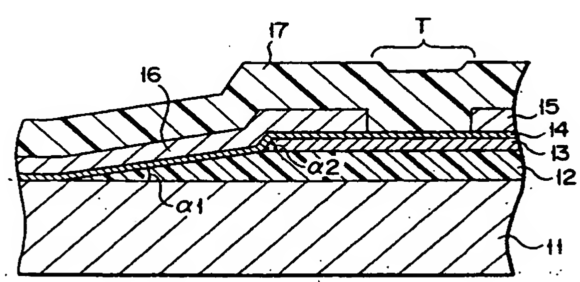

F I G. 2

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 8862

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 877 644 (WU ET AL) * the whole document * *	1,5,6,9	B 41 J 2/335
A	WO-A-9 001 374 (ROGERS CORPORATION) * abstract; figures 1-3 * * * page 4, line 8 - page 6, line 14 * *	1,5,6,9	
A	EP-A-0 309 146 (AM INTERNATIONAL INC.) * column 4, line 2 - line 34; figure 2 * *		
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 559 (M-905)(3907) 12 December 1989 & JP-A-01 232 067 (HARUO TANMACHI ET AL) 18 September 1989 * abstract * *	1,3,4	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
B 41 J B 23 K

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	09 December 91	ROBERTS N.

CATEGORY OF CITED DOCUMENTS

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